# FULLERENE FORMATION IN A HELIUM-CARBON PLASMA

A. Huczko[1], H. Lange[1] and P. Byszewski[2,3]

[1]Laboratory of Plasma Chemistry, Department
 of Chemistry, University of Warsaw,
 02-093 Warsaw, Poland
[2]Institute of Vacuum Technology,
 00-241 Warsaw, Poland
[3]Institute of Physics PAN,
 02-668 Warsaw, Poland

**Abstract.** Carbon arc characteristics was studied
during fullerene synthesis in a helium plasma at
13.3 kPa. Resulting soot contained more than 20
wt% of crude   fullerenes at arc current (d.c.
mode of operation) within 65-70 A. However, the
highest production rate of fullerenes was obtained
at higher arc current (ca 80 A) due to a distinct
increase of erosion rate of graphite electrodes.
Application of a well-stabilized d.c. power source
seems to favor the process overall efficiency.

## 1. Introduction

One of the greatest open questions in the field of
fullerenes - a rapidly growing subfield of physical and
organic chemistry [1,2] - is the understanding how such
compact, closed structures form so efficiently from carbon
species. Though various authors have shown some possible
channels regarding reaction mechanism [3] there exists still
a lack of knowledge of the fullerene-forming processes.
Obviously, this knowledge is essential when scaling-up the
synthesis. Various techniques of fullerene production have
been developed but the electric arc approach was the winner
in the competition for maximum reaction yield and ease of
implementation. Up to now, the process optimization is based
on the relationship between the process yield and operation-
al variables. However, since the fullerenes are being formed
in a high-temperature zone it seems reasonable to study the
relationship between the arc phenomena, the plasma charac-
teristics and the reaction yield. Thus the present work was
aimed at the carbon arc characteristics during fullerene
synthesis for the d.c. mode of arc operation. Such an appro-

ach can provide new insights into the fullerene formation mechanistics and, to our knowledge, has never been tried before. In the study the relationship between some operational variables (power input, the type of power supply) and fullerene formation yield was investigated.

## 2. Experimental

All tests were carried out in the experimental system presented schematically in Fig. 1 under the operational parameters which are considered to be the most favorable regarding the fullerene yield [4], i.e. in a carbon arc plasma with graphite (spectral carbon) electrodes 6 mm in diameter and 100 mm long. The interelectrode gap was kept close to 1 mm due to the application of a 3-directions actuator. The arc operated in helium and the pressure equal to 13.3 kPa was maintained. The system was fed with a direct current (between 50 and 110 A) since our earlier studies [5] showed this mode of arc operation as being superior in comparison to the a.c. feeding. Two various power sources were used (a rectifier welding supply RWS and a welding motor generator WMG) with a completely different I-U time profiles of EMF [6] since it was shown earlier [7] that the d.c. EMF source characteristics can influence the arc phenomena. The voltage-current characteristics of the arc discharge (for both power supplies) is shown in Fig. 2. As we found out, the electrode configuration (interelectrode gap) more than the power source characteristics influences the U-I relationship so there is only a slight difference for both power supplies.

Strong UV radiation from the arc plasma may be expected under experimental conditions. As a matter of fact, the formation of ozone in the atmosphere surrounding the vicinity of reactor's observation ports was detected (as a result of atmospheric oxygen irradiation) what forced us to install the additional ventilation system.

During a run the arcing of electrodes results in anode erosion. The sooty deposit condensed on the reactor walls was processed by a conventional extraction after collection [8]. Thus, the crude fullerene content in the soot could be obtained.

## 3. Results and Discussion

Depending on the arc current the soot resulting from the anode erosion manifests itself as a bright luminosity within the plasma flame and as a smoke emission at the anode tip. It may be suggested that the visibility of the cloud seen during the rapid volatilization of graphite must be a direct evidence that the dimension of the carbon nanobodies (resulting from the carbon vapor aggregation) is at least of the order of the wavelength of the light scattered from the

aerosol, i.e. ca 500 nm or more. Thus all carbon nanostructures of that size are thought to be formed close to the plasma zone. The temperatures in the interelectrode gap are within the boiling point of graphite (4700 K) [5]. In front of the anode a dense carbon vapor layer is formed which temperature, with an increasing current, can exceed the boiling temperature. The corresponding local dynamic pressure increases significantly, too. The surface temperatures of the electrodes were measured with an optical pyrometer and the results are shown in Table 1.

Table 1. Results of temperature measurements of electrode surface (RWS power supply).

| Arc current [A] | Temperature [K] | | |
|---|---|---|---|
| | Cathode edge | Anode edge | Anode tip |
| 50 | 1950 | 2500 | 2950 |
| 60 | 2200 | 2650 | 3150 |
| 70 | 2550 | 2900 | 3800 |
| 80 | 2400 | 2850 | 3300 |

As expected, much higher temperatures were recorded for the anode. The surface temperature of electrodes obviously increases with a raising current. Within 60-70 A the anode face temperature approaches the sublimation point of graphite. One should mention that the pyrometric readings of the temperature may be disturbed by carbon vapor evolving from the electrode surface. Specially at current higher than 70 A some irregularities in temperatures are definitely related to the dense carbon fumes evolving from the arc zone what makes the pyrometric readings unreliable.
On the base of the material balance the anode erosion rates were estimated as a function of a power density at the anode tip (assuming a 50 per cent transfer of input power to the anode face [9]) - Fig. 3. As expected, a distinct increase of erosion for both power sources was observed with the current increase, specially for I higher than 65 A (power density higher than 20 W/mm$^2$). It confirms that under those conditions the sublimation point of graphite is reached and further power input increase results (almost linearly) in the higher mass of the vaporized material only. Higher erosion rates were obtained for WMG power supply, specially at higher power input. The specific energy requirement SER (calculated by dividing arc power by erosion rate) for graphite vaporization was also calculated and the results vs. anode erosion rate are shown in Fig. 4. SER is, as

expected, inevitably much higher than the heat of vaporiza-
tion of graphite since only a part of the energy input is
available at the anode tip for the vaporization process. As
a matter of fact, the lowest thermodynamically possible SER
(calculated from the heat of graphite sublimation) is within
$10^{-3}$ kJ/mg. As it is evident from Fig. 4 much lower SER was
obtained for arc current above 65 A, specially for WMG
supply.
For all runs performed the resulting soot was collected and
its condensation rate was estimated. At lower power input
the convection prevails in the system resulting in higher
condensation rate for a soot condensing on reactor cover
(comparing to reactor walls). However, for arc current above
80 A a strong anode flame of carbon vapor is directed
towards the cathode and, as a result, higher condensation
rates are obtained for reactor walls.
Fig. 5 shows the quantitative results regarding fullerene
synthesis, i.e. the fullerene content in collected soot and
the production rate of fullerenes (calculated on the base of
the data presented in Fig. 3 and 4). As one can see, the
highest fullerene content (exceeding 20 wt%) and the highest
production rate (much higher for WMG power supply) were not
obtained at the same arc current. This phenomena can be
explained by the fact that the decrease in fullerene content
(above 60-70 A) is lower that the increase of a soot
production rate.
Thus the application of a well-stabilized current source
(WMG power supply) favors the overall process efficiency
what is in line with our previous conclusions [5] regarding
the comparison of a.c and d.c. arc feeding.

**Acknowledgment**

**References**

[1] H.W. Kroto, Angew. Chem. Int. Ed. Engl., **31**, 111, 1992.
[2] W. Kraetschmer, D.R. Huffman, Carbon, **30**, 1143, 1992.
[3] R.F. Curl, Trans. R. Soc. London, A, **19**, 343, 1993.
[4] A. Huczko, Chem. News (in Pol.), **47**, 241, 1993.
[5] H. Lange, P. Byszewski, A. Huczko, P. Ukalski, 3rd Eur.
    Con. Therm. Plasma Prc., Aachen, Germany, 36, 1994.
[6] A. Huczko, H. Lange, P. Byszewski, submitted for
    publication (J. Phys. Chem.).
[7] X.K. Wang, X.W. Lin, V.P. Dravid, J.B. Ketterson, R.P.H.
    Chang, Appl. Phys. Lett., **66**, 427, 1995.
[8] A. Huczko, H. Lange, P. Byszewski, Pol. J. Appl. Chem.,
    No.4, 1994.
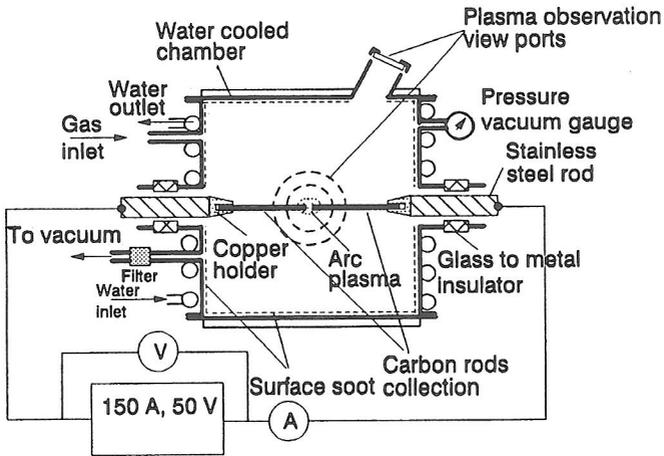[9] A.J. Wickens, Chem. and Ind., No.7, 316, 1976.
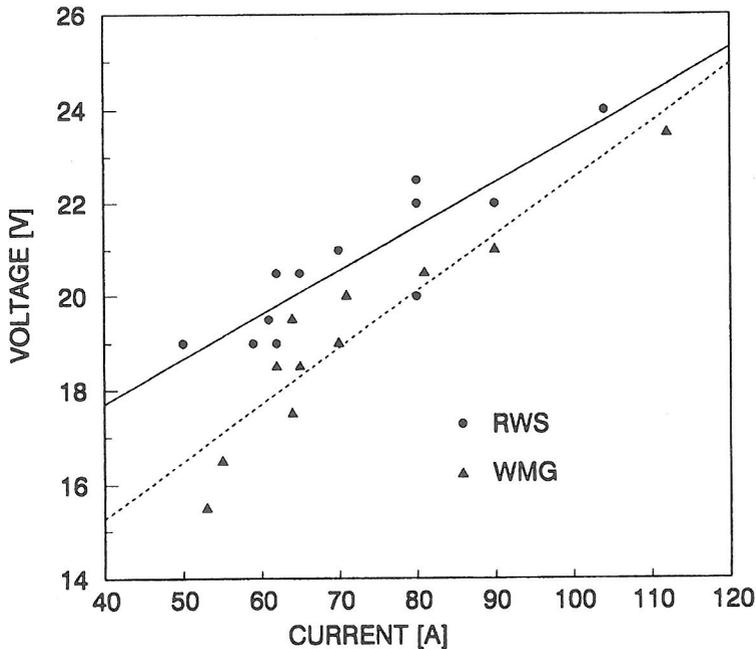
Fig. 1 Experimental setup.



Fig. 2 Voltage-ampere characteristics of arc
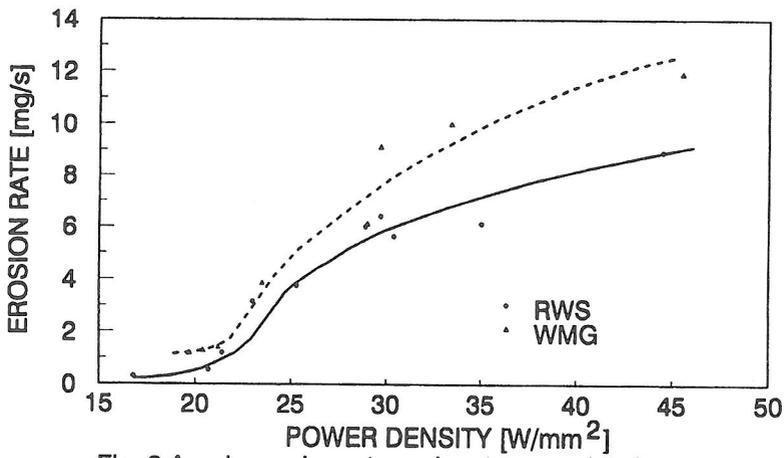discharge for RWS and WMG power supplies.

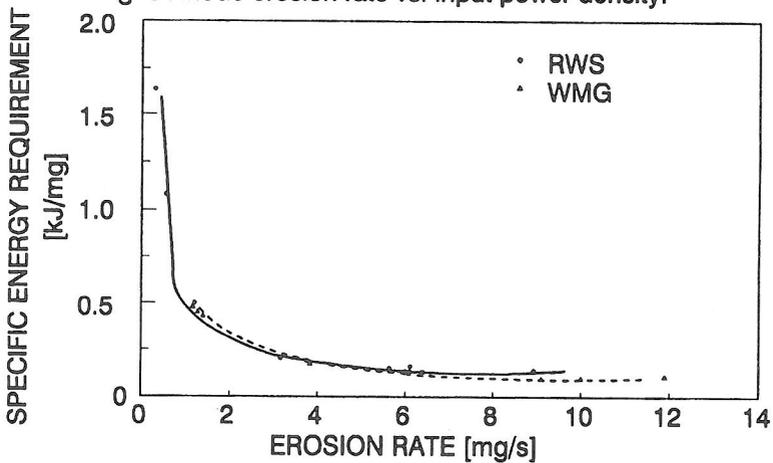Fig. 3 Anode erosion rate vs. input power density.


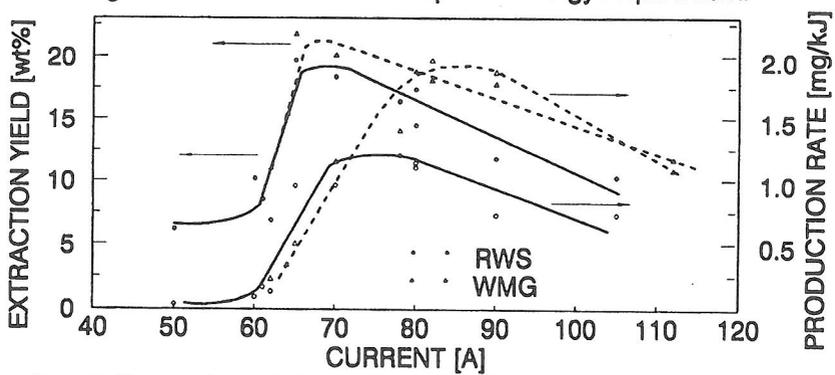
Fig. 4 Anode erosion rate vs. specific energy requirement.



Fig. 5 Extraction yield and production rate vs arc current.